possess different coordinations, $H_2O(1)$ having a flat pyramidal threefold one, and $H_2O(2)$ a distorted tetrahedral one. The three different $O-H\cdots S$ bonds of the structure are approximately at right angles to the acceptor NCS groups ($O\cdots S-C = 89-112°$) and have similar dimensions (Table 2). $H\cdots S$ and $O\cdots S$ distances are slightly shorter than for the 'average' $O-H\cdots S$ bond between water and sulphur, for which $O\cdots S = 3.324$ Å was reported (Mereiter, Preisinger & Guth, 1979). Two $O-H\cdots S$ bonds similar in lengths to those of the title compound have been found by neutron diffraction in $Mg_2S_2O_3.6H_2O$ ($O\cdots S = 3.26$ and 3.25 Å, $H\cdots S = 2.28$ and 2.34 Å; Elerman, Fuess & Joswig, 1982). Judged from its length, the $O(1)-H(12)\cdots O(2)$ bond seems to be weaker than the $O-H\cdots S$ bonds of the structure.

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Structure of Iron(II) Molybdenum(IV) Oxide Fe₂Mo₃O₈*

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Abstract. $Fe_2Mo_3O_8$, $P6_3mc$, $a = 5.7732$ (6), $c = 10.0542$ (11) Å at 298 K with $Z = 2$ giving $d_{calc} = 6.03$ Mg m^{-3}. The structure was refined to $R_F = 0.029$ for 966 reflections observed with Mo $K\alpha$ radiation. The compound is isostructural with $Zn_2Mo_3O_8$ with Mo—Mo distances of 2.5296 (6) Å inside the clusters and 3.2436 (6) Å from cluster to cluster. The so-called $FeMoO_3$ (JCPDS pattern #19-611) is likely to be $Fe_2Mo_3O_8$.

Introduction. Large crystals of the phase $Fe_2Mo_3O_8$ were grown in the course of a study of mixed oxides in the $FeO-MoO_2$ system (Strobel, McAlister & Le Page, 1982). This substance was first synthesized by McCarroll, Katz & Ward (1957) who prepared a series of isostructural oxides $M_2^{II}Mo_3^{IV}O_8$ ($M =$ Mg, Mn, Fe, Co, Ni, Zn and Cd). They indexed the $Fe_2Mo_3O_8$ powder pattern in the space group $P6_3mc$ with $a = 5.782 \pm 0.005$ and $c = 10.046 \pm 0.010$ Å by similarity with the single-crystal studies of the Zn and Mg analogues. The

JCPDS file contains no data on $Fe_2Mo_3O_8$, but the observed powder pattern from crushed crystals obtained in the present study fitted quite well the JCPDS pattern #19-611 following the description by Rusakov, Novokhatskii, Lenev & Savinskaya (1965) of a hexagonal phase $FeMoO_3$ with cell parameters $a = 4.67$ and $c = 15.03$ Å. A single-crystal study was therefore undertaken in order to investigate the interesting structural features of $Fe_2Mo_3O_8$, especially the Mo_3 clusters, and to clarify the ambiguity about its identification.

The diffraction intensities of a 0.36 mm diameter sphere of $Fe_2Mo_3O_8$ were measured at 298 K. Graphite-monochromatized Mo $K\alpha$ radiation generated at 50 kV and 8 mA was used in a $\theta/2\theta$ scan with line-profile analysis (Grant & Gabe, 1978). A total of 1265 intensity measurements were made up to $2\theta = 90°$. They reduced to 969 unique reflections (including Friedel equivalents), of which 966 had $I_{net} > 3\sigma(I_{net})$ and were considered to be observed. The agreement $\langle\Delta I\rangle/\langle I\rangle$ of the measurements of the symmetry-related intensities was 1.1%. Only 41 of the 100 unique

measurements of the systematic absences were unobserved. The high percentage of observation among both the valid reflections and the systematic absences is due to multiple reflection arising from the considerable reflectivities of many planes in this compound. We performed rotations about the diffraction vectors for the worst violations of the space-group absences. For some rotation angles, their intensities became unobserved, confirming the diffraction symbol $P..c$. A spherical absorption correction was performed due to the high absorption coefficient $\mu = 110.7\ cm^{-1}$. The cell parameters $a = 5.7732\ (6)$, $c = 10.0542\ (11)$ Å were refined from the setting angles of 24 reflections with 2θ angles larger than 70° using $\lambda(Mo\ K\alpha_1) = 0.70932$ Å.

The atomic positions in the isostructural compound $Zn_2Mo_3O_8$ (Ansell & Katz, 1966) were used as a starting point for the refinement. All atomic positions were refined with anisotropic thermal motion by full-matrix least squares except the z coordinate of the Mo atom which was set at 0.25 in order to fix the origin. An extinction correction was included (Larson,

Table 1. Positional parameters and equivalent isotropic thermal parameters

E.s.d.'s refer to the last digit printed. B_{eq} is the arithmetic mean of the principal axes of the thermal ellipsoid.

	x	y	z	B_{eq} (Å²)
Mo	0.14605 (3)	$-x$	0.25 (fixed)	0.171 (3)
Fe(1)	$\frac{1}{3}$	$\frac{2}{3}$	-0.04810 (14)	0.350 (19)
Fe(2)	$\frac{1}{3}$	$\frac{2}{3}$	0.51301 (13)	0.270 (18)
O(1)	0	0	0.3906 (7)	0.29 (8)
O(2)	$\frac{1}{3}$	$\frac{2}{3}$	0.1470 (7)	0.33 (9)
O(3)	0.4883 (4)	$-x$	0.3629 (4)	0.33 (3)
O(4)	0.1671 (4)	$-x$	0.6344 (4)	0.373 (24)

Table 2. Distances (Å) and angles (°) in Fe₂Mo₃O₈

The e.s.d.'s on all the angles are 0.2°. The digits on the upper right and upper left of a bond length are respectively the bond multiplicity at the cation and at the anion.

	O(1)	O(2)	O(3)	O(4)
Mo	3 / 2.033 (5) / 1	3 / 2.140 (3) / 1	2 / 2.073 (3) / 2	2 / 1.956 (4) / 2
Fe(1)		1 / 1.962 (7) / 1	1 / 1.995 (5) / 3	
Fe(2)			1 / 2.163 (4) / 3	1 / 2.062 (4) / 3

O(1)–Mo–O(2)	164.9	O(2)–Fe(1)–O(3)	116.6
O(1)–Mo–O(3)	90.0	O(3)–Fe(1)–O(3)	101.5
O(1)–Mo–O(4)	100.6		
O(2)–Mo–O(3)	78.6	O(3)–Fe(2)–O(3)	76.5
O(2)–Mo–O(4)	89.6	O(3)–Fe(2)–O(4)	172.1
O(3)–Mo–O(3)	80.7	O(3)–Fe(2)–O(4)	97.1
O(3)–Mo–O(4)	90.9	O(4)–Fe(2)–O(4)	88.6
O(3)–Mo–O(4)	166.6		
O(4)–Mo–O(4)	95.3		

Table 3. Powder pattern for Fe₂Mo₃O₈ calculated for Cu $K\alpha$ radiation using the present single-crystal results

The pattern is complete for intensities of 5 or more up to 84° 2θ. $A2$ on the right of the indices indicates an α_2 line while a + indicates that several reflections contribute to this line and the indices correspond to the most intense contributor. The powder pattern reported by Rusakov et al. for FeMoO₃ using Co $K\alpha$ radiation is shown on the right.

	Fe₂Mo₃O₈			FeMoO₃			
d (Å)	I/I_1	$h\ k\ l$		d (Å)	I	$h\ k$	l
5.024	99	0 0 2		5.03	s	0 0	3
4.471	22	1 0 1					
3.542	100	1 0 2		3.55	s	0 1	2
2.7828	32	1 0 3		2.78	w	1 0	4
2.5022	83	1 1 2 +		2.50	s	0 0	6
2.4251	75	2 0 1		2.42	m	1 0	5
2.2383	19	2 0 2		2.24	m	1 1	2
2.0036	42	2 0 3		2.01	s	2 0	1
1.8894	6	2 1 0 +					
1.8568	13	2 1 1		1.86	w	2 0	3
1.7724	21	2 0 4		1.77	m	2 0	4
1.6456	31	2 1 3 +		1.65	m	0 0	9
1.5889	6	1 0 6					
1.5819	16	3 0 2					
1.5780	8	3 0 2 A2					
1.5667	41	2 0 5		1.57	s	2 0	6
1.5629	21	2 0 5 A2					
1.4432	24	2 2 0		1.45	m	1 1 8:1 2	3
1.4396	12	2 2 0 A2					
1.3876	7	2 2 2 +		1.39	m	1 0 10	
1.3772	5	2 1 5					
1.3367	4	3 1 2		1.34	w	1 1	9
1.2517	7	2 2 4		1.25	m, br	1 1 12:1 2	7

1970). Scattering factors for neutral atoms as well as absorption coefficients were taken from International Tables for X-ray Crystallography (1974). The final residuals were $R_F = 0.029$, $wR_F = 0.033$. Counting-statistics weights were used throughout. The agreement between calculated and measured Bijvoet differences confirms that the point group is correct, that the absolute orientation of the polar sixfold axis is correct and that the crystal is not twinned by merohedry. The atomic positional parameters are listed in Table 1, the bond distances and angles in Table 2 and the calculated powder pattern in Table 3.*

Discussion. The description of $Zn_2Mo_3O_8$ by McCarroll et al., (1957) applies to $Fe_2Mo_3O_8$ with Mo and one Fe atom in octahedral sites while the other Fe atom is in a tetrahedral site. The Zn compound is the only one in the series to have been studied with diffractometer data (Ansell & Katz, 1966). Their crystal was quite small

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* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36534 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

and only 253 measurements were refined by least squares. The agreement of the results is quite good with Mo—Mo approaches of 2·5296 (6) Å inside the Mo_3 clusters and 3·2436 (6) Å with the closest Mo in the neighbouring cluster for the Fe compound, as compared with 2·524 (2) and 3·235 (2) Å for the Zn compound. The average Mo—O distances are, respectively, 2·051 (2) and 2·03 (1) Å with similar distortions around the Mo atom. The distortions around the Fe^{2+} seem to be marginally larger than those around Zn^{2+} possibly because Fe^{2+}, a high-spin $3d^6$ ion, has an unsymmetrical occupation of the t_{2g} levels while Zn^{2+} has a filled $3d$ shell.

The similarity of the present calculated powder pattern of $Fe_2Mo_3O_8$ with the JCPDS pattern #19-611 raises serious doubts about the existence of the phase $FeMoO_3$ described by Rusakov et al. (1965). Such a compound has not been found in a phase study of the Fe—Mo—O system at 1413 K (Abe, 1972), although its melting point is reportedly 1853 ± 30 K. The density measured for '$FeMoO_3$' agrees well with those observed and calculated for $Fe_2Mo_3O_8$ by McCarroll et al. (1957), respectively 6·00, 6·04 and 6·02 Mg m^{-3}. On the other hand, 5·13 formulae of $FeMoO_3$ would be required to explain the measured density and this value seems unlikely. In our opinion, the JCPDS pattern

#19-611 is an incorrectly indexed pattern of $Fe_2Mo_3O_8$. In the same way, the pattern #18-845 for $MgMoO_3$ described by the same authors should be re-examined: the pattern can be indexed using the cell parameters for $Mg_2Mo_3O_8$ and the observed densities agree (5·20 and 5·30 Mg m^{-3}).

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Structure of Sodium Hydrogenphosphite

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Abstract. $Na_{0.5}H_{2.5}PO_3$, $M_r = 92·99$, trigonal, $P\bar{3}c1$, $a = 5·908$ (2), $c = 9·554$ (4) Å, $Z = 4$, $U = 288·8$ Å^3, $D_c = 2·14$, $D_m = 2·135$ Mg m^{-3}, $\mu(Mo\ K\alpha) = 0·767$, $\mu(Ag\ K\alpha) = 0·392$ mm^{-1}. $R = 0·022$ ($R_w = 0·033$) for 843 reflexions $[I > 3\sigma(I)]$ measured with Ag $K\alpha$ radiation, $R = 0·022$ ($R_w = 0·044$) for 884 reflexions $[I > 3\sigma(I)]$ measured with Mo $K\alpha$ radiation, 23 parameters were refined. Each P tetrahedron is connected to three other P tetrahedra by hydrogen bonds so that infinite sheets of composition $[H_{2.5}PO_3]_n^{(n/2)-}$ are formed in the structure parallel to the xy plane. The sheets are held together by the Na^+ ions.

Introduction. The study of the title compound was undertaken as part of an investigation of the $Na_2HPO_3–H_3PO_3–H_2O$ system. The compound $NaH_2PO_3.H_3PO_3$ was first described by Lefforge & Hudson (1952) and Ebert & Škvára (1964) found the exact conditions for its crystallization.

A crystal of dimensions 0·45 × 0·45 × 0·75 mm sealed in a glass capillary was mounted on a Picker FACS-1 diffractometer. Cell dimensions were calculated from the setting angles of 15 reflexions measured at ±2θ using Mo $K\alpha$ radiation. Reflexions were measured out to 2θ = 100° with Zr-filtered Mo $K\alpha$ radiation. A second data set (2θ$_{max}$ = 80°) was collected with Pd-filtered Ag $K\alpha$ radiation. In both cases an ω–2θ scan was used with a step length of 0·04° and a counting time of 1 s step^{-1}. The scan widths were (3·0 + 0·692 tan θ)° for Mo $K\alpha$ radiation

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